LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-PROC-217713

Evidence for Groundwater Contamination Vulnerability in California#s Central Valley

J.E. Moran, R. Leif, B.K. Esser, M.J. Singleton

December 13, 2005

2006 California Plant and Soil Conference
Visalia, CA, United States
February 7, 2006 through February 8, 2006

UCRL-PROC-217713

Evidence for Groundwater Contamination Vulnerability in California's Central Valley

Jean E. Moran
L-231, P.O. Box 808 Lawrence Livermore National Laboratory, Livermore, CA 94550;
phone (925)423-1478; fax (925)422-3160; e-mail: moran10@llnl.gov

Roald Leif
L-396, P.O. Box 808 Lawrence Livermore National Laboratory, Livermore, CA 94550;
phone (925)422-2469; fax (925)422-5673; e-mail: leif1@llnl.gov

Bradley Esser
L-231, P.O. Box 808 Lawrence Livermore National Laboratory, Livermore, CA 94550;
phone (925)422-5247; fax (925)422-3160; e-mail: esser1@llnl.gov

Michael J. Singleton
L-231, P.O. Box 808 Lawrence Livermore National Laboratory, Livermore, CA 94550;
phone (925)424-2022; fax (925)422-3160; e-mail: singleton20@llnl.gov

INTRODUCTION

The California Water Resources Control Board, in collaboration with the US Geological Survey and Lawrence Livermore National Laboratory, has implemented a program to assess the susceptibility of groundwater resources. Advanced techniques such as groundwater age-dating using the tritium-helium method, extensive use of oxygen isotopes of the water molecule ($\delta^{18}O$) for recharge water provenance, and analysis of common volatile organic compounds (VOCs) at ultra-low levels are applied with the goal of assessing the contamination vulnerability of deep aquifers, which are frequently used for public drinking water supply. Over 1200 public drinking water wells have been tested to date, resulting in a very large, tightly spaced collection of groundwater ages in some of the heavily exploited groundwater basins of California. Smaller scale field studies that include shallow monitoring wells are aimed at assessing the probability that nitrate will be transported to deep drinking water aquifers. When employed on a basin-scale, groundwater ages are an effective tool for identifying recharge areas, defining flowpaths, and determining the rate of transport of water and entrained contaminants. De-convolution of mixed ages, using ancillary dissolved noble gas data, gives insight into the water age distribution drawn at a well, and into the effective dilution of contaminants such as nitrate at long-screened production wells. In combination with groundwater ages, low-level VOCs are used to assess the impact of vertical transport. Special studies are focused on the fate and transport of nitrate with respect to vulnerability of aquifers in agricultural and formerly agricultural areas.

BACKGROUND AND METHODS

The basic premise for using groundwater age to establish vulnerability is that young groundwater has been transported to a well capture zone relatively rapidly from the earth's surface. Most contaminants have been introduced in shallow zones by human activity in the past 100 years, so younger groundwater is more likely to have intercepted contamination. On

the other hand, old groundwater is likely to be isolated from the contaminating activities that are ubiquitous in modern urban and agricultural environments. The age measures the time since the water sample was last in contact with the atmosphere. Well water samples are always a mixture of water molecules with an age distribution that may span a wide range. The reported groundwater age is the mean age of the mixed sample, and furthermore, is the age only of the portion of the water that contains measurable tritium. Groundwater age dating has been applied in several studies of basin-wide flow and transport (Solomon et al., 1992, Ekwurzel et al., 1994, Manning et al., 1995). A groundwater age analysis requires measurement of tritium, a radioactive isotope (half life 12.3 yrs) of hydrogen that is part of the water molecule, and of its daughter product, dissolved ^{3}Helium. Dissolved noble gas samples are collected in copper tubes, which are filled without bubbles and sealed with a cold weld in the field. Dissolved noble gas concentrations are measured at LLNL after gas extraction on a vacuum manifold and cryogenic separation of the noble gases. Tritium samples are collected in 1L glass bottles. The ratio of ^{3}He to ^{4}He is measured on a VG5400 mass spectrometer. After correcting for minor sources of ^{3}He not related to ^{3}H decay (Aesbach-Hertig et al., 1999; Ekwurzel et al., 1994), the measurement of both tritium and its daughter product ^{3}He allows calculation of the initial tritium present at the time of recharge, and mean apparent ages can be determined from the following relationship:

$$\text{Groundwater Apparent Age (years)} = -17.8 \times ln\,(1 + {}^{3}\text{He}_{trit}/{}^{3}\text{H})$$

Groundwater without detectable tritium recharged the aquifer more than about 50 years ago. Ages in the range of 0 to 50 years are reported with an analytical uncertainty of about +/- 1 year. This technique is particularly useful for identifying a component of groundwater that has been recharged in the last 15 years.

Just as tritium provides a time marker for groundwater recharge, so can chemicals that have been widely used only in post-industrial times. The presence of volatile organic compounds such as gasoline compounds, organic solvents, and applied agricultural chemicals is an indication that the sampled water recharged since the onset of intense human development. In this study, these compounds are measured with a reporting limit of 5 parts per trillion – well below routine monitoring and regulatory limits. When examined at sub-part-per-billion concentrations, these VOCs serve as useful environmental tracers, since they have a near ubiquitous presence at low concentrations near the earth's surface due to common human activities. Their presence in groundwater is indicative of a component of post-industrial aged water. Thus, the interpretation of VOC detections in this study is not with regards to health or regulatory concerns, but rather as another tracer of recent groundwater recharge. And, since the number of years the different VOCs have been in common use differs – over 100 years for disinfection by-products, 50 to 60 years for heavy use of the solvents, and only 10 to 15 years for the gasoline additive MtBE, their presence or absence can be used to mark the time since recharge.

Surface nitrogen loading has dramatically increased in the last 70 years, making groundwater ages a useful first approach to vulnerability assessment. Fertilizer usage in California had doubled from 1950 to 1980 after which it leveled off at approximately 600,000 tons per year. Nationwide, nitrogen fertilizer use in the country increased over 300 percent from 1960 to

1988, with very little change in crop acreage and only a 40 percent increase in overall farm production. Field studies have shown that approximately one third of applied fertilizer is lost to leaching using older application methods. Furthermore, changes in fertilizer application may not be seen in groundwater for up to 60 years because of retention and cycling of fertilizer N in soil.

Transport of nitrate is important not only in evaluating the susceptibility of a pristine aquifer to nitrate contamination, but also in evaluating the time scale over which source controls will affect nitrate levels in a contaminated aquifer. In evaluating both uncontaminated and contaminated aquifers, the assimilative capacity of the aquifer for nitrate loading through denitrification also needs to be taken into account. Many of the studies of denitrification in the saturated zone have been sited in shallow and young groundwater systems affected by industrial or wastewater contamination. Groundwater pumped from California drinking water supply wells is generally deeper and older. The age of deep groundwaters allows time for oxygen depletion by aerobic microbial oxidation of dissolved organic carbon (or another appropriate electron donor). In the absence of a systematic survey of ambient oxygen levels in California groundwaters, oxygenation in deep drinking water aquifers cannot be assumed. Although alluvial aquifers in the Central Valley are often well oxygenated, examples of low oxygen waters do exist in both shallow and deep aquifers. In this study, denitrification is examined by analyzing the dissolved gas composition and stable isotopes of nitrogen and oxygen in nitrate. The end product of denitrification is nitrogen; this dissolved nitrogen can be quantified in groundwater once a correction is made for nitrogen from entrained air. Denitrification drives the isotopic composition of the residual nitrate to higher $\delta^{15}N$ and $\delta^{18}O$ values. The stable isotopes of nitrogen are more strongly fractionated during denitrification than oxygen, leading to a trajectory on a $\delta^{18}O$ vs. $\delta^{15}N$ diagram with slope of 0.5 (see review by Kendall, 1998).

FIELD STUDY RESULTS

An example of the application of the tritium-helium age dating method from the GAMA program is shown in figure 1. Forty drinking water wells from the Bakersfield, CA area produce groundwater with tritium-helium ages that span nearly the entire range of the method, from 2 to 50 years. Recharge of diverted Kern River and other captured and imported water sources in unlined canals that traverse Bakersfield leaves the dominant imprint on the pattern observed in groundwater age. Wells adjacent to canals, near the center of the urban area, produce groundwater that has predominantly recharged in only the last seven years, while downgradient wells in the outlying areas produce exclusively older groundwater that recharge more than 40 years ago. The coarse-grained alluvial sediments that make up the Kern River fan likely allow significant vertical transport in the areas of artificial recharge.

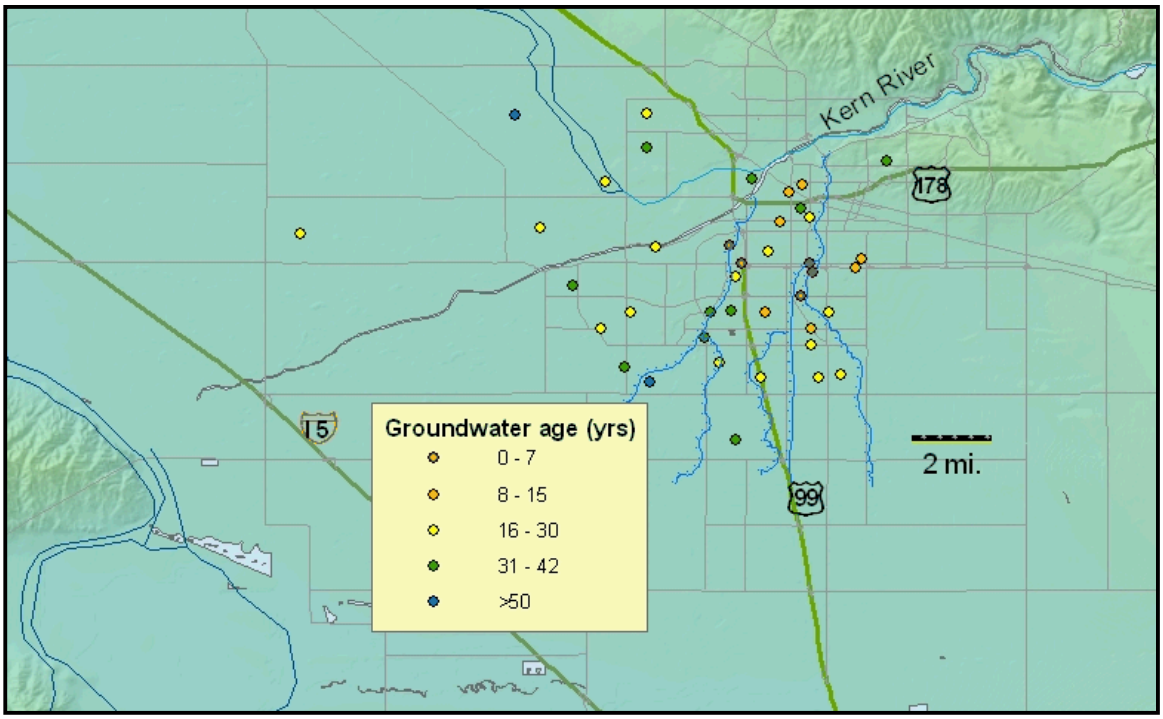


Figure 1. Tritium-helium groundwater ages show a pattern of increasing age toward the margins of the study area. Very recently recharged groundwater is produced at several wells along canals, in the center of the study area.

In the Bakersfield area, active recharge in an area of historical tetrachloroethylene (PCE, a solvent used in dry cleaning and industrial processes) contamination leads to entrainment of PCE in many of its drinking water wells (Figure 2). All Central Valley study areas visited so far show evidence for vulnerability with respect to transport of contaminants, especially PCE, to deep aquifers tapped for drinking water. This finding is in sharp contrast to results from Coastal aquifers such as Santa Clara Valley, where, despite the presence of a large number of contaminant plumes, deep wells are most frequently completely free of any VOC detections (Table 1).

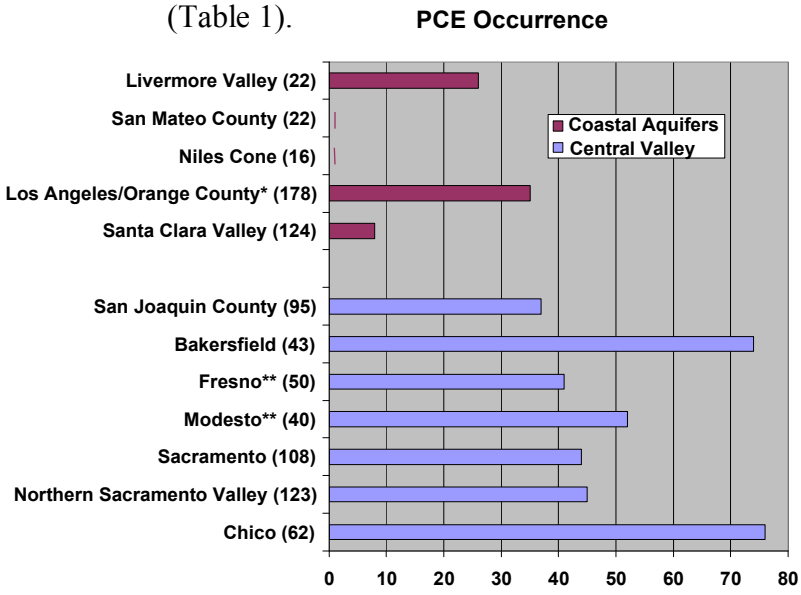


Figure 2. A comparison of percent of wells with PCE occurrence in GAMA focus areas reveals the ubiquity of low-level PCE in public supply wells in Central Valley study areas. Numbers in parentheses are the number of public supply wells sampled and analyzed for low-level PCE in the study area. Chico results are included in the overall results shown for the northern provinces. *USGS results from Shelton et al., 2001, with a lower reporting limit of 10 ng/L. **USGS results from Wright et al., 2004, with a lower reporting limit of 10 ng/L.

	Coastal Basins[1] N=194	Central Valley Basins[2] N=338
No VOCs[3]	105 (54%)	48 (14%)
MtBE	29 (15%)	87 (25%)
PCE	18 (9%)	166 (49%)
$CHCl_3$	68 (35%)	252 (74%)

Table 1. Low-level VOCs results comparison for Coastal and Central Valley basins.

1 Includes Santa Clara Valley, Basins of San Mateo County (San Mateo Plain, Westside Basin and Coastside Basin), Livermore-Amador Basin, and Niles Cone (Fremont, CA)

2 Includes Bakersfield, Chico and surrounding northern Sacramento Valley, Sacramento, and San Joaquin County urban areas (Stockton, Lodi, and Manteca); wells from areas outside of alluvial basins are not included on this table

3 Samples had <RL (reporting limit of 5 ng/L) for MtBE, chloroform, bromodichloromethane, chlorodibromomethane, bromoform, tetrachloroethylene (PCE), trichloroethylene (TCE), benzene, toluene, ethylbenzene, xylene, dibromochloropropane, and ethylene dibromide

Two contrasting field studies illustrate the utility of direct examination of denitrification indicators to assess contamination vulnerability and the fate and transport of nitrate (Figure 3a and 3b). In the Llagas basin of southern Santa Clara County, high nitrate concentrations are observed in shallow-screened wells, but not in wells screened exclusively below 200 ft. (with one exception; Figure 3a). Since groundwater is also stratified with respect to dissolved oxygen (deep water being devoid of DO), denitrification could be the cause of the observed sharp decrease in nitrate levels. However, no dissolved excess nitrogen was found in these wells, and stable isotopes of nitrate are indicative of a synthetic fertilizer source unaltered by denitrification. In this basin, deep groundwater is relatively invulnerable to shallow contamination because of physical barriers to vertical groundwater flow. Tritium concentrations below detection from deep wells support the notion that vertical transport is limited in the most contaminated areas of the Llagas Basin.

In contrast, results from a dairy site in Kings County show conclusively that denitrification is taking place in the saturated zone (Figure 3b). High concentrations of excess nitrogen are found in groundwater with low nitrate concentrations and stable isotopes of nitrate are shifted to higher values along a line of slope ½. Field studies utilizing age-dating, source attribution, and denitrification characterization are a powerful approach to designing appropriate nitrate management plans and to assessing the effectiveness of nitrate management plans. At the Kings County dairy site, nitrate loading is mitigated by denitrification, and nitrate will not be transported to the deep aquifer used for drinking water supply. In the Llagas Basin, deep wells have not yet been affected by nitrate from the contaminated shallow zone, and may not be for several decades.

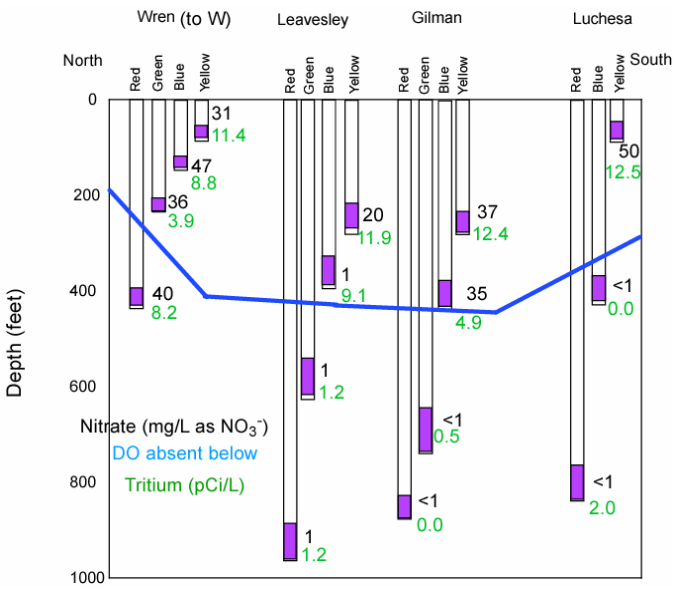
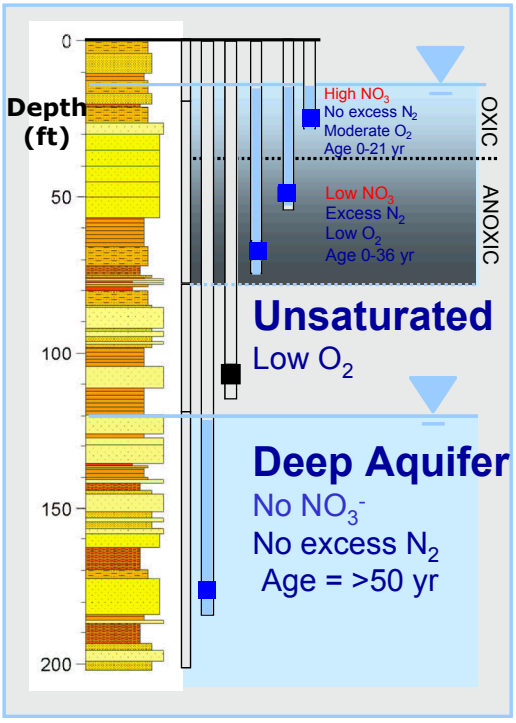


Figure 3 a. Schematic cross section showing screened intervals (in purple) of nested monitoring wells in Gilroy. Groundwater is stratified with respect to nitrate, tritium, and dissolved oxygen (blue line signifies depth below which dissolved oxygen is near-zero).



Multi-level wells:
Excess N_2 by MIMS, Age by ^3H-^3He

Figure 3b. Cross-sectional view of groundwater and aquifer characteristics at a Kings County dairy site. Denitrification in the shallow aquifer mitigates transport of N to deep aquifers.

Literature Cited:

Aeschbach-Hertig, W., Peeters, F., Beyerle, U., and Kipfer, R. (1999) Interpretation of dissolved atmospheric noble gases in natural waters. Water Resources Research, v. 35, p. 2779-2792.

Ekwurzel, B., Schlosser, P., Smethie, W.M., Plummer, L.N., Busenberg, E., Michel R.L., Weppernig, R., and Stute, M. (1994) Dating of shallow groundwater - Comparison of the transient tracers $^3H/^3He$, chlorofluorocarbons, and ^{85}Kr. Water Resources Research, v. 30, p. 1693-1708.

Kendall, C. Tracing nitrogen sources and cycling in catchments, In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. 1998. Elsevier Science, Amsterdam, pp. 519–576.

Manning, A.H., Solomon, D.K., Thiros, S.A. (2005) $^3H/^3He$ age data in assessing the susceptibility of wells to contamination. Groundwater, V. 43(3), doi:10.1111/j.1745-6584.2005.0028.x

Solomon, D.K., Poreda, R.J., Schiff, S.L., and Cherry, J.A. (1992) Tritium and helium-3 as groundwater age tracers in the Borden aquifer. Water Resources Research, v. 28, p. 741-755.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.